CYCLO-ALIPHATIC EPOXIDE BASED PHOTO CURED GELLED ELECTROLYTES FOR SECONDARY Li BATTERY APPLICATIONS. ELECTROCHEMICAL KINETIC STUDIES.

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Abstract

Cyclo aliphatic epoxide based thin gelled films prepared by UV photo curing were characterized electrochemically. Ethylene carbonate (EC) mixed with different organic liquids in different volume ratios were used as solvents. General composition of the electrolyte was cyc1o aliphatic epoxide (being sold under the trade name "ENVIBAR" by Union Carbide) 10-28 w%, Polyethylene Oxide (200,000 M.W.) 4-10 w%, $LiAsF_6$ 6-22 w% and mixed solvents (of different volume ratios) 80-40 w%. Thin gelled films were formed on Li electrodes and subjected to electrochemical studies. Typical values of bulk electrolyte conductivity and interracial resistance obtained from a-c impedance and d-c measurements at room temperature are $2x10^{-3}$ S cm^{-1} and 3.2 Ohms respectively. Charge /discharge characteristics of the cells of the type Li/electrolyte/TiS_2 were evaluated. Cathode utilization was only 33% of the total capacity.

Introduction

Solid electrolytes which exhibit high ionic conductivity have generated, in recent years, wide-spread interest as potential electrolyte materials for a variety of applications including solid-state batteries, chemical sensors and fuel cells[1]. The pioneering work of Armand et al[2] and others[3] led to the development of solid polymer based electrolytes for battery applications. However, these materials do not exhibit appreciable room temperature conductivity. Several different approaches including the incorporation of liquids in solid polymer structures to improve the room temperature ionic conductivity are being studied. For example less than two decades ago Feuillad and Perche[4] have reported the use of polyvinyl acetal and poly acrylonitrile based ion-conductive membrane gels as separator in Li-CuS batteries. Recently, Watanabe et al[5] reported that the room temperature Li^+ conductivity of poly vinylidene fluoride/or poly acrylonitrile containing $LiClO_4$ and ethylene carbonate (the so-called "gelled" electrolyte) can be varied between 10^{-4} and 10^{-8} S cm^{-1} depending upon the composition. These were formed by heating the mixture of polymer, $LiClO_4$ and EC (ethylene carbonate) above 100"C and casting the viscous fluid on molds to form gelled electrolytes. In recent years radiation curing technique is being extensively used to form gelled electrolytes for Li battery applications Among the patents cited in reference 6 the following two patents #5,006,431 and #5,102,752 are the most relevant to our work. At the Jet Propulsion

Laboratory, as apart of an on going secondary Li battery research effort, we have initiated preliminary electrochemical studies on the photo cured cyclo-aliphatic epoxide based gelled electrolytes. We report below the results of our study on the electrochemical properties of the cyclo-aliphatic epoxide based gelled electrolyte containing $LiAsF_6$, PEO and EC based mixed solvents.

Experimental

Battery grade $LiAsF_6$ purchased from LaRoche Industries Georgia, USA and the solvents ethylene carbonate (EC), propylene carbonate (PC), diethyl carbonate (DEC), dimethyl carbonate (DMC) purchased from Mitsubishi, Japan and Triglyme purchased from Aldrich, USA were used as received. The cyclo aliphatic epoxide based photo curable polymer (being sold under the name "EN_VIBAR") and the photo initiator "6990'" were received from Union Carbide as free samples. Several film compositions: ENVIBAR 10-28 w%; Li salt 6-22 w%; poly ethylene oxide (PEO) (M. W. 200,000) 4-10 w%; EC based mixed solvents (different volume ratios) 80-40 w% and three drops of 6990: were investigated. The films were formed as follows. Appropriate amounts of solvent mixture, Li salt and PEO were weighed in to a 50 ml glass beaker and stirred inside an Argon filled glove box over night followed by the addition of ENVIBAR and 6990. The viscous fluid was further stirred for 1 hour and then transferred to a "dry-room". The viscous fluid was painted on to a freshly prepared Li electrode which was photo

cured to form thin films . Typically the thickness of the polymer film was around 100 μm. The films were subjected to a series of electrochemical studies. Standard micro-computer controlled electrochemical equipment were used in all of our measurements. Of the several films prepared with different compositions all of them were not investigated in detail since they were either mechanically too weak (if the solvent content exceeds 70 w%) or the room temperature conductivity was $<10^{-4}$ S/cm (if the solvent content is <50 w%) . The film that exhibited both good mechanical integrity and room temperature conductivity was ENVIBAR (14 w%), PEO (4 w%), $LiAsF_6$ (16 w%) and mixed solvent (66 w%). This composition was studied in detail as a function of composition of the mixed solvents (Table-l).

Results and Discussion

ELECTROLYTE STUDIES

Under appropriate conditions the fundamental electrochemical parameters such as bulk conductivity, charge transfer resistance (R_{ct}) of the electrolytes can be evaluated using a-c and d-c measurements. A-C and d-c electrochemical studies were made on electrolyte films sandwiched between two lithium or stainless steel (ss) electrodes (symmetrical configuration) or between Li and SS (asymmetrical configuration) to characterize the bulk and interracial properties of the films. In Table-1 is given the list of electrolytes investigated in this study. Although a

thorough and systematic study was made on all of these electrolytes, for the sake of clarity, electrochemical measurements are described for ENVIBAR 14 w%; $LiAsF_6$ 16 w%; poly ethylene oxide (PEO) (M. W. 200,000) 4 w%; EC/DEC (50/50 v%) 66 w%. The composition is denoted as "GEL-l"

a-c measurement:

SYMMETRICAL CELL

In Fig. 1 is shown, for GEL-1 in a symmetrical cell, the NyQuist plot in the frequency regime 100 kHz - 5 Hz, The electrolyte room temperature bulk conductivity and R_{ct} obtained from this plot are $2x10^{-3}$ S cm^{-1} and 3.2 Ohms respectively. The a-c measurements made as a function of time indicate that while the bulk conductivity remains stable the R_{ct} increases initially to 4.5 Ohms and straddles there after. In general, the bulk resistivity and the R_{ct} are smaller for EC/DEC solvent based electrolytes than for EC/DMC and EC/Triglyme (Table-l). Among the EC/DEC combination the composition with equal volumes of EC and DEC (50/50 v%) is marginally better than the rest. In Fig. 2 is shown the NyQuist plot for GEL-1 sandwiched between two well polished ss electrodes, The "blocking contact" can in principle yield results that indicate the purity of the interface. If the interface is a perfect capacitor the NyQuist plot should be a straight line perpendicular to the x-axis. At very high frequencies, since the capacitative impedance $(1/\omega C)$ is near zero, the a-c measurement should yield the bulk electrolyte

resistance. The plot in Fig. 2 is almost perpendicular to the x-axis indicating the capacitative nature of the interface and the absence of electronic conductivity in the cell. The electrolyte bulk conductivity computed from this plot is 1.46×10^{-3} S/cm which is close to the value obtained above.

d-c measurement:

ELECTROCHEMICAL POTENTIAL WINDOW

The electrochemical potential window of the electrolyte (GEL-1) was measured against Li as the reference electrode. The description of the cell is given else where[7]. In Fig. 3 is shown the current-voltage plot for GEL-1. The electrolyte appears stable in the potential regime between 1.5 and 4.5 v vs. Li, with very little breakdown current or leakage current. The wide potential window may permit the use of high voltage cathodes such as $LiCoO_2$ and $LiMnO_2$ in conjunction with this electrolyte. However, for our preliminary evaluation we have chosen TiS_2 as the cathode.

LINEAR POLARIZATION. SYMMETRICAL CELL(Li/GEL-1/Li)

Butler-Volmer, equation which describes the various processes that govern and control electrochemical reactions can be written for a single-electron process as

$$i = i_o\{e^{[(1-\alpha)FE/RT]} - e^{[-\alpha FE/RT]}\}$$

At very small voltage excursions i.e., $FE/RT \ll 1$ the above

equation reduces to $i = i_o FE/RT$. The effective exchange current density and hence R_{ct} can be calculated from the IR-free polarization plots near E =0 using the above equation. Linear polarization measurement between 5 mv to -5 mv was made . In Fig.4 is shown a typical linear polarization plot. R_{ct} computed from this plot is 4.5 Ohms which is in agreement with the R_{ct} value obtained from the a-c measurement. The variation in R_{ct} as a function of time is similar to that of the R_{ct} from the a-c measurement.

Li PLATING/STRIPPING EFFICIENCY (Li/GEL-1/ss)

Li plating/stripping efficiency was computed both potentiostatically and galvanostatically.

Potentiostatic Method:

In the potentiostatic measurement the voltage was scanned at 2 mv/see, 500 mv on each side of the rest potential. Initially, the potential was scanned negative of the rest potential for plating Li on ss and then to positive of the rest potential for stripping Li from the ss electrode. In Fig. 5 is shown on such plot (after 50 cycles) and the computed plating/stripping efficiency is 89% (after 50 cycles) which although is not attractive for battery applications could be improved with other anode materials such as carbon.

Galvanostatic Method:

Known amount of Li was galvanostatically plated on ss surface followed by stripping a part of it. This cycle was repeated several times. Using the following equation[8] the average Li plating/stripping efficiency was computed.

$$X = \{q_c - [Xq_i - q_f]/n\}q_c$$

where X is the average cycling efficiency per cycle, and

q_c= charge plated or dissolved per cycle

q_i= charge involved in the initial deposition

q_f= charge involved in the final dissolution of Li and

n = total number of cycles.

The amount of Li plated and stripped in every cycle is given in Table-2. In the first cycle 1.0 C (q_i) was plated and finally the total coulombs (q_f) of Li stripped from the ss electrode was 1.5 C. The plating/stripping efficiency is close to 90% which is comparable to the value obtained from the potentiostatic method.

CELL STUDIES: $Li/GEL\text{-}1/TiS_2$

The cathode was a composite cathode consisting of TiS_2, PEO and $LiAsF_6$. Appropriate amounts of TiS_2, PEO and $LiAsF_6$ were taken so that the final composition of the composite cathode was TiS_2:PE0 1:1 volume ratio and PEO:$LiAsF_6$ = O:Li ratio of 8:1. A 2"x2" section was cut and was used as the cathode. From the weight of the composite cathode the capacity was computed as 60 mAh.

Lithium was used as anode. Stainless steel foils were used as support and for electrical contact for cathode and anode. The cell was sealed under vacuum. One of the finished cells is shown in Fig.6. The cell was subjected to cyclic voltammetric (CV) measurement before the charge/discharge studies. In Fig.7 is shown the cv trace at room temperature. Two well defined diffusional peaks, one corresponding to intercalation of Li ion in to TiS_2 at around 2.7 v and the other deintercalation of Li ion from the lithiated TiS_2 lattice at around 2.1 v, are observed. In Fig. 8 is shown the charge/discharge characteristics of the above cell at different rates. In the 1st cycle the discharge capacity was only 20 mAh and in subsequent cycles the capacity didn't increase. The very low cathode utilization could be due to several factors including unoptimized cathode composition, thickness, and thin film morphology. Further, no gelling agent was added to the composite cathode which could lead to higher resistivity at room temperature which may in turn lead to poor cathode utilization. Currently cathode improvement studies are underway.

Conclusions

Thin films of different compositions in the range ENVIBAR 10-28 w%, PEO 4-10 w%, $LiAsF_6$ 6-22 W% and mixed solvents 80-40 w% were photo cured on Li electrodes and were characterized electrochemically. The bulk conductivity and R_{ct} of films of composition: ENVIBAR 14 w%; Li salt 16 w%; poly ethylene oxide

(PEO) (M. W. 200,000) 4 w%; EC/DEC (50/50 v%) 66 w%. are $2x10^{-3}$ S cm^{-1} and 3.2 Ohms respectively. Lithium plating/stripping efficiency was only 90%. Although the measurement of the plating/stripping efficiency as described above does not exactly reflect the situation that exists in a real cell where a cathode replaces the ss electrode, this figure might give the lower limit of Li turn-over efficiency in a real cell. Thin cells containing 60 mAh composite TiS_2 cathode, 300 mAh Li anode and 100 μm thick gelled electrolyte were fabricated. The cathode utilization was only 20 mAh. The low cathode utilization efficiency could be due, among other things, to unoptimized cathode composition, thickness etc. Optimization of cell design and cathode composition are currently underway.

Acknowledgement

The work described here was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration.

References

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Figure Captions:

Figure 1. A-C Behavior (NyQuist plot) of Li/GEL-1/Li at Room Temperature. A-C Ferquency was Varied from 100 kHz to 5 Hz. V_{p-p}=5 mv.

Figure 2. A-C Behavior (NyQuist plot) of ss/GEL-1/ss at Room Temperature. A-C Ferquency was Varied from 100 kHz to 5 Hz. V_{p-p}=5 mv.

Figure 3. Electrochemical Behavior of GEL-1 Sandwiched Between two Well Polished ss Electrodes. Scan Rate = 2 mv/sec.

Figure 4. Linear Polarization Plot of GEL-1 Sandwiched Between Li Electrodes. Scan Rate = 2 mv/sec.

Figure 5. Lithium Plating/Stripping Behavior of Li/GEL-1/ss at Room Temperature. Scan Rate = 2 mv/sec.

Figure 6. Photograf of the Li/GEL-1/TiS_2* Cell. Cell Design = Flat. Cathode Capacity = 60 mAh. Anode = Lithium of 300 mAh. Electrode Size 2"x2". * = Composite Cathode.

Figure 7. Cyclic Voltammetric Behavior of Li/GEL-1/TiS_2* at Room Temperature. Scan Rate = 5 mv/sec. * = Composite Cathode.

Figure 8. Charge/Discharge Characteristics of the cell in Fig. 7 at Room Temperature.

Table-1. Bulk Conductivity and R_{ct} of Gelled Electrolytes With Different Solvent Compositions.

Electrolyte Composition: ENVIBAR 14 w%; Li salt 16 w%; (PEO) (M. W. 200,000) 4 w%; Solvent Mixture (Different compositions V%)66 w%.

Base Poly.	Solv-$LiAsF_6$	Composition v/v %	Bulk Cond. (S/cm)	R_{ct} (Ω cm^2)
ENVIBAR	EC + PC	20/80	10^{-3}	200
"	"	50/50	$2X10^{-3}$	180
"	"	80/20	$3X10^{-3}$	120
"	EC +DMC	50/50	$3X10^{-4}$	900
"	EC+Triglyme	50/50	$5X10^{-4}$	890
"	EC + DEC	20/80	10^{-3}	150
"	"	50/50	$2X10^{-3}$	90
"	"	80/20	10^{-3}	120

Table-2. LITHIUM PLATING/STRIPPING EFFICIENCY

CELL CONFIGURATION: Li/GE*-1/SS

* = ENVIBAR(14 w%), PEO(4 w%), EC/DEC(66 w%), $LiAsF_6$(16 w%)

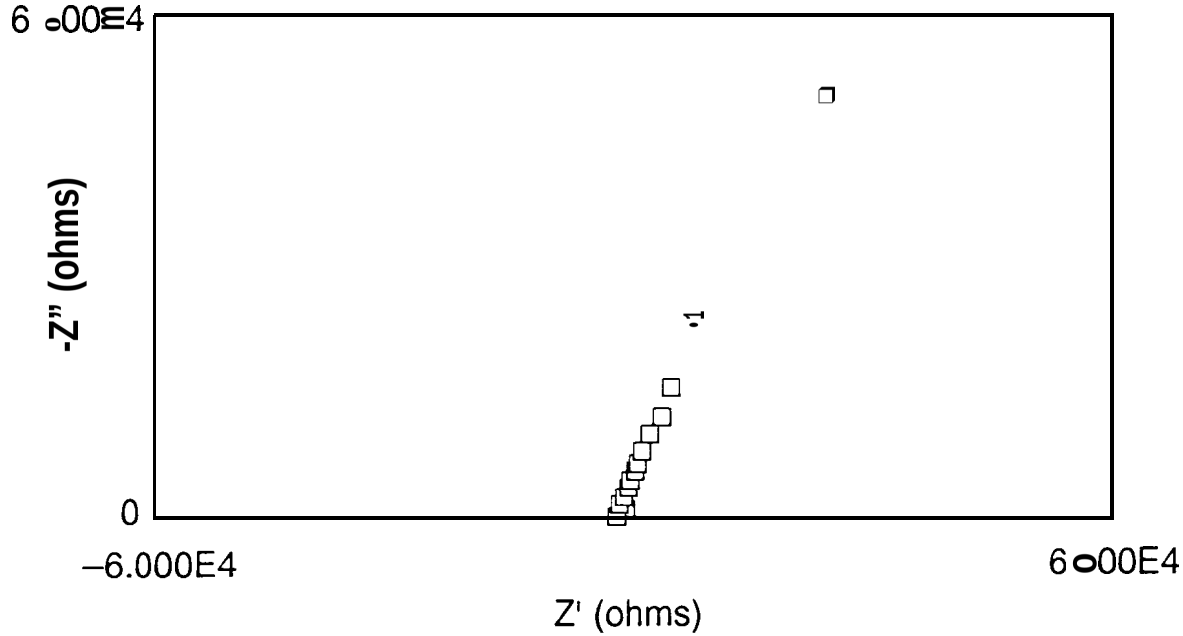
SS = STAINLESS STEEL

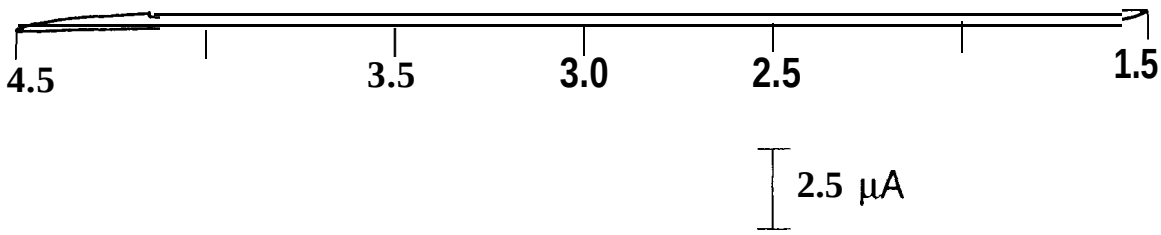
ELECTRODE AREA = 0.7 cm^2

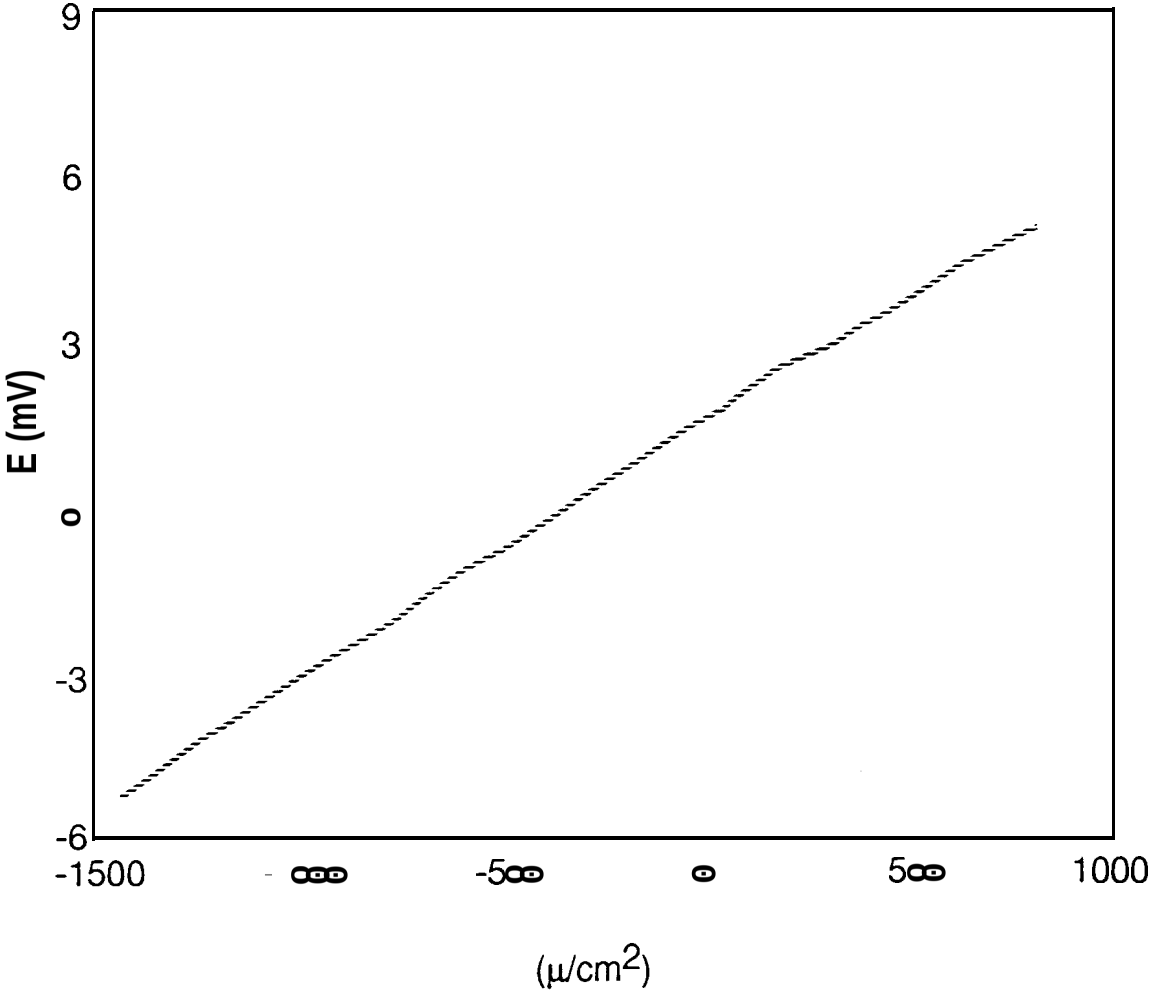
ELECTROLYTE THICKNESS = 0.009 cm

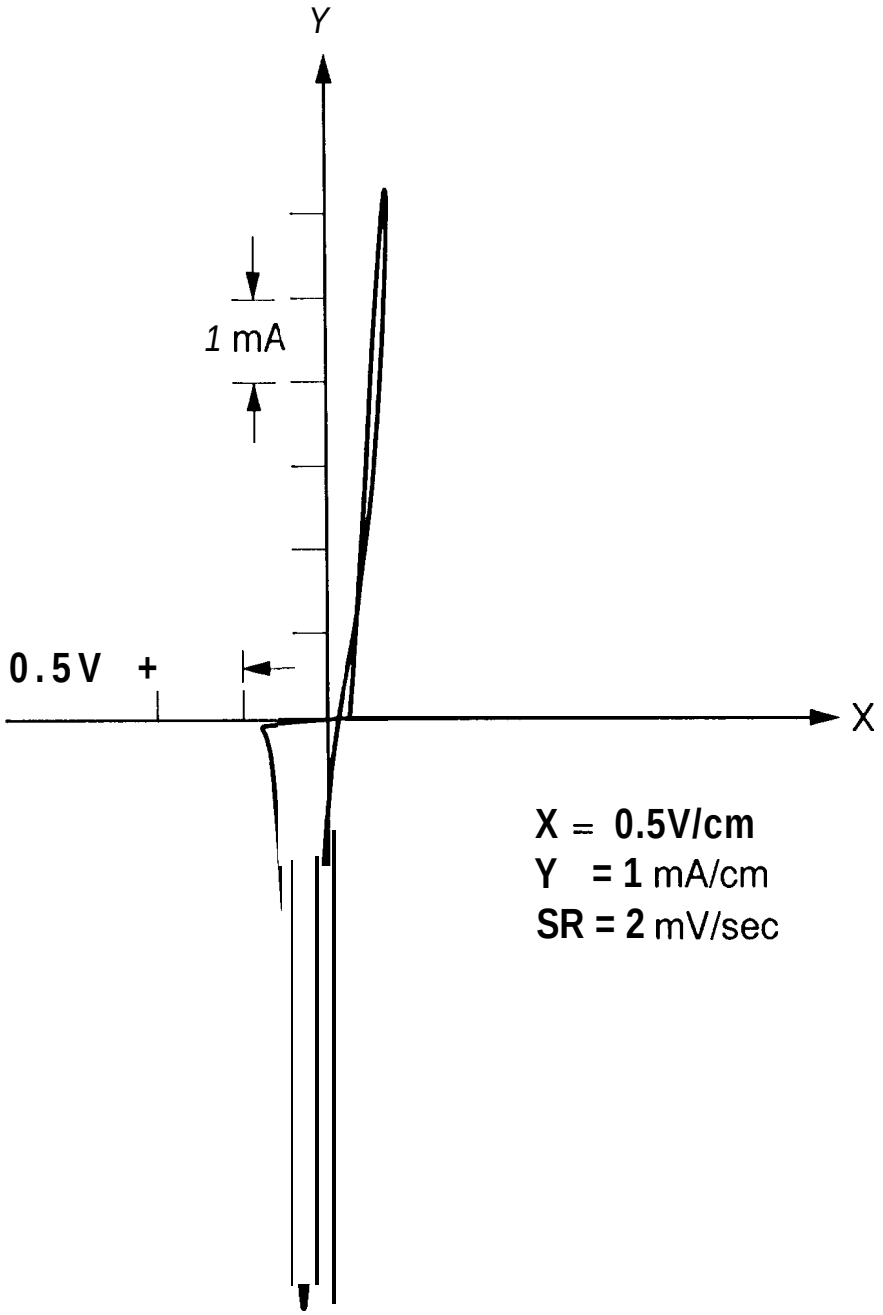
CYCLE #	PLATING (C)	STRIPPING (C)
1	1.00	0.50
2	1.00	0.50
3	1.25	0.75
4	1.00	0.50
5	0.50	1.00
6	1.00	0.50
7	0.50	0.50
8	1.00	1.00
9	0.50	1.65

2.5
0
0
Z (ohms)
−Z'' (ohms)

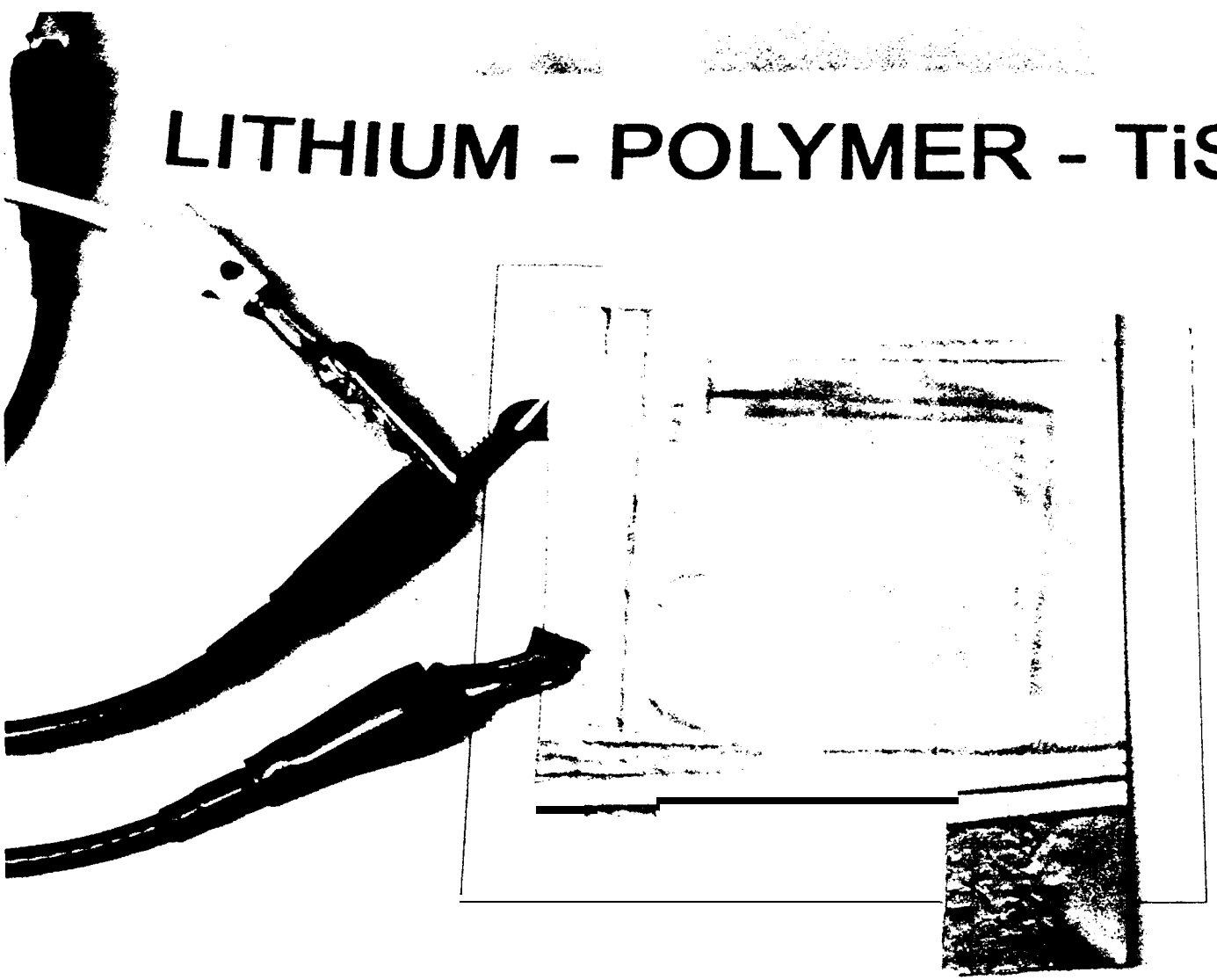

6.000E4
-Z" (ohms)
0
–6.000E4
6.000E4
Z' (ohms)


4.5
3.5
3.0
2.5
1.5
2.5 μA
V vs. Li

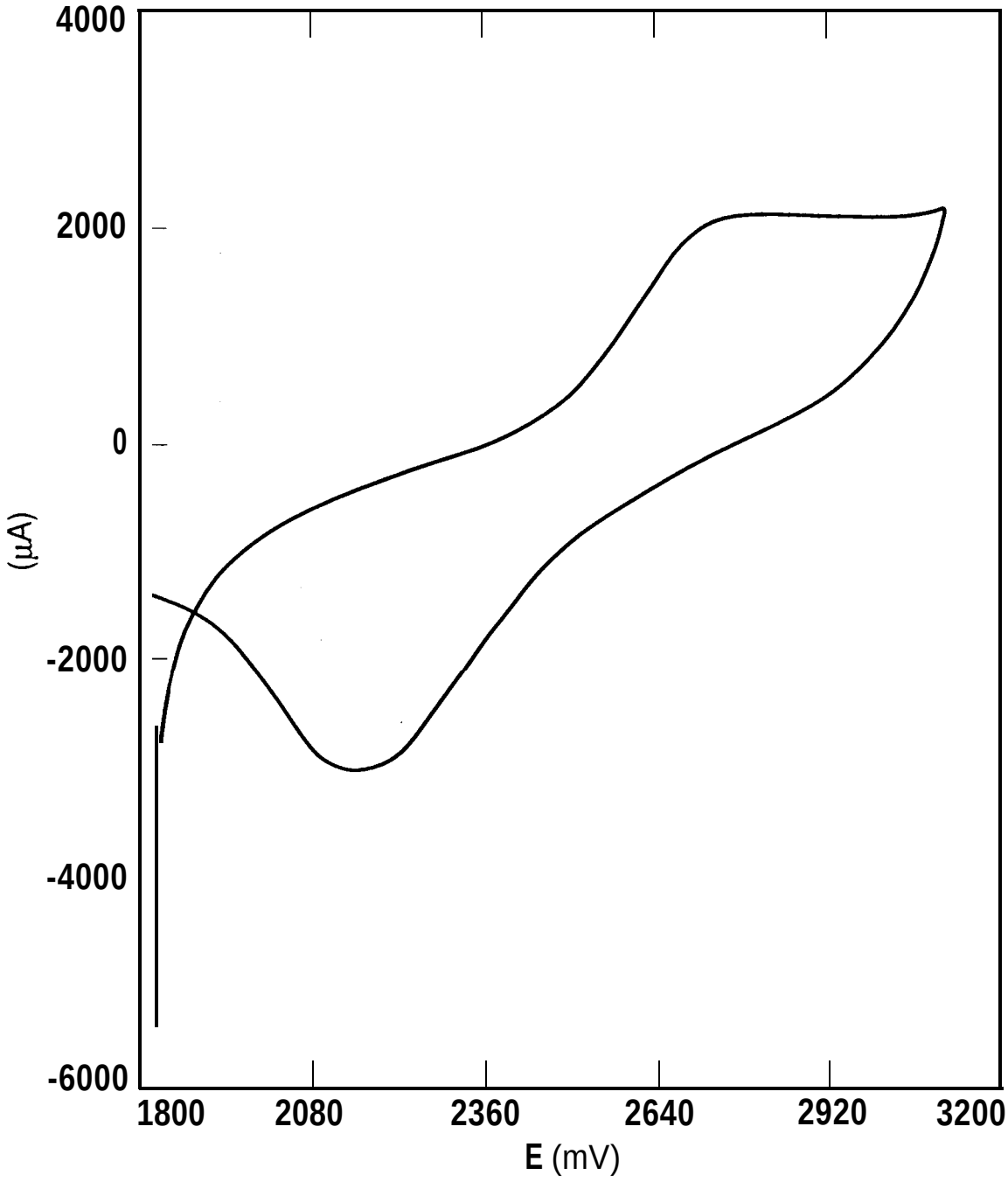

9
6
3
0
-3
-6
E (mV)
-1500
-5
0
5
1000
(μ/cm2)

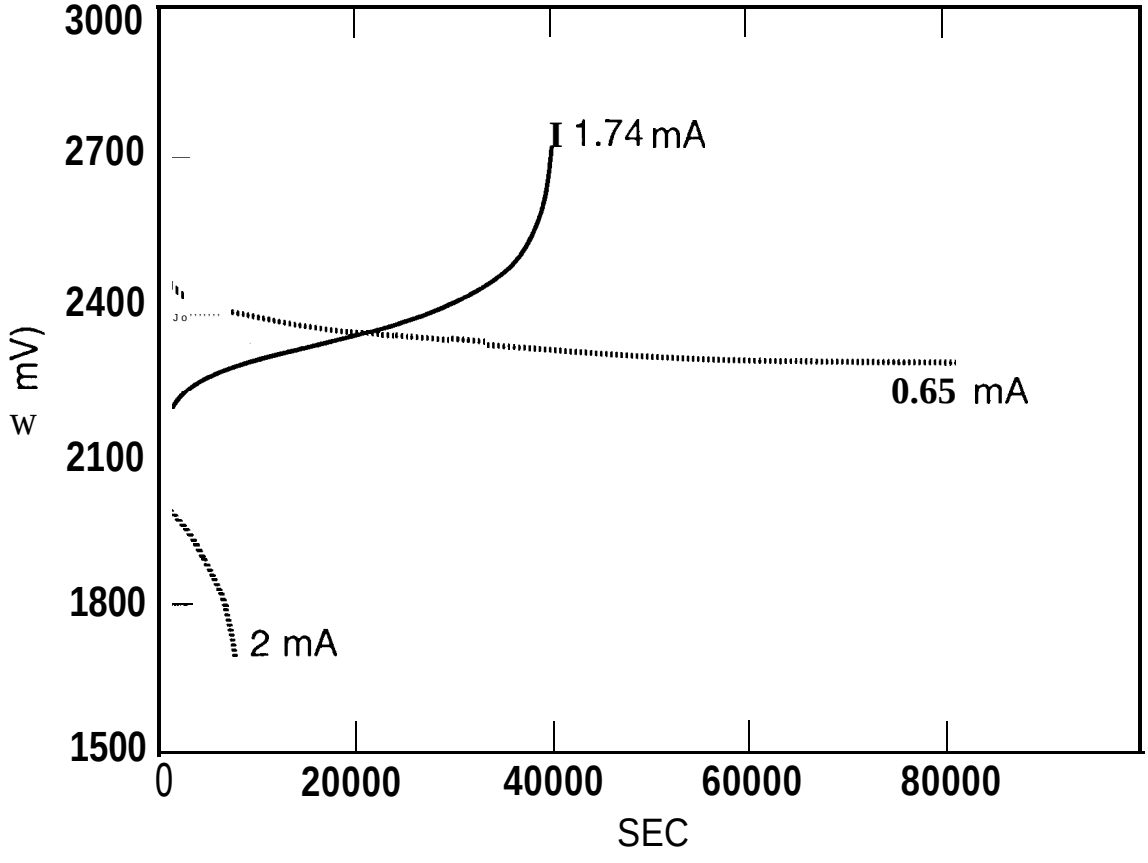

Y
1 mA
0.5V +
X
X = 0.5V/cm
Y = 1 mA/cm
SR = 2 mV/sec

LITHIUM - POLYMER - TiS_2 CELL



- POLYMER: GELLED ELECTROLYTE
- CAPACITY: 60 MILLIAMPERE-HOURS


4000
2000
0
-2000
-4000
-6000
(μA)
1800
2080
2360
2640
2920
3200
E (mV)


3000
2700
2400
2100
1800
1500
mV)
W
I 1.74 mA
0.65 mA
2 mA
0
20000
40000
60000
80000
SEC